

# EXTRUSION FOAMING OF POLY(STYRENE-CO-ACRYLONITRILE) USING SUPERCRITICAL CARBON DIOXIDE

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## INTRODUCTION

Polymeric foams are cellular materials with wide applications in insulating, packaging and automobile industry because of their low weight, high strength-to-weight ratio, good insulating properties and high impact strength. Furthermore, the steady increase of oil prices in recent years led to an increase of plastic costs. Producing plastic foams can thus be an alternative to decrease the amount of resin used, as long as the foam keeps acceptable mechanical properties<sup>1</sup>. In this context, microcellular foams with a controlled cell morphology exhibit better mechanical properties over conventional plastic foams with larger cells. It is also noteworthy that foam stiffness is directly related to foam density and cell regularity<sup>2</sup>. While traditional foaming processes have relied on hydrocarbon or fluorocarbon (CFC's) blowing agents, efforts are now devoted to use more environmentally friendly gases.

In this study, we used supercritical CO<sub>2</sub> as a physical blowing agent in a specifically designed single-screw extruder. This gas was chosen for several reasons: it is cheap, non-toxic, inert, non-flammable and it has easily attainable supercritical conditions (31.1 °C, 73.8 bar). Moreover, CO<sub>2</sub> under supercritical conditions dissolves into a high number of non polar polymer matrixes to form a single-phase polymer/gas solution. When the gas is injected at the middle of the screw, it dissolves into the melted polymer and forms a single-phase polymer/gas solution. The melt viscosity is highly decreased during this step, due to the plasticization effect of the gas. When the polymer/gas solution reaches the die, a sudden decrease of pressure occurs. This induces a thermodynamic instability inside the polymer, generating a large quantity of bubbles (nucleation). The cell growth is observed until the foam is frozen (when  $T < T_g$ ).

The morphology of the resulting foam depends on several parameters. The cell density is mostly a function of the gas concentration inside the polymer matrix and the pressure drop rate<sup>3</sup>, whereas the cell size is relied to the temperature of the system, the time allowed for the cell growth, the state of supersaturation, the stress applied to the polymer matrix and the gas/polymer rheology<sup>4</sup>.

This study reports on the continuous production of poly(styrene-co-acrylonitrile) (SAN) foams with supercritical carbon dioxide as foaming agent in a modified single-screw extruder, which has never been described in the literature yet. Attention was paid to the influence of the temperature profile in the extruder on cell morphology and foam density. Cooling of the foam at the exit of the extrusion line was also envisaged as it is proved that this treatment improves the foam morphology by freezing the foam earlier, in order to avoid cell coalescence<sup>5,6</sup>.

## I - MATERIALS AND METHODS

### Materials

SAN with an acrylonitrile content of 25 wt % (Luran<sup>®</sup> 358N, BASF), was used in these experiments. CO<sub>2</sub>, used as foaming agent, was provided by Air Liquide (99.995 %).

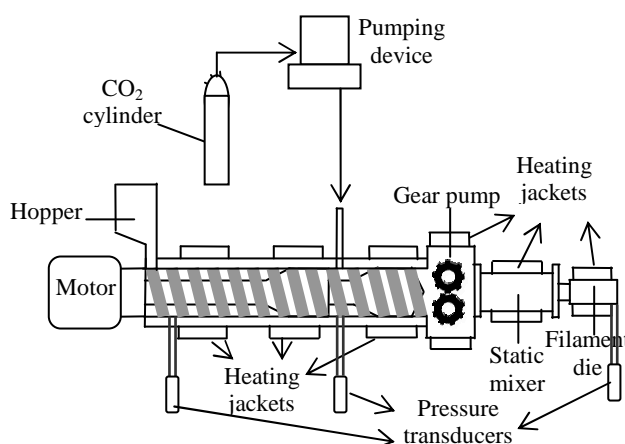


Figure 1 : Experimental setup used for the continuous production of SAN microcellular foams.

### Experimental setup

A schematic diagram of the experimental equipment is shown in figure 1. Basically, it consists of a single-screw extruder from Brabender<sup>®</sup> (19/25D) coupled with a gear pump. A multi-stage screw with one feed section, two compression sections and one mixing section was especially designed for this application. The polymer is introduced through the hopper and melted in the first compression section of the screw. Carbon dioxide is compressed with a syringe pump (ISCO 260D) and injected into the mixing zone at a constant volumetric flow. In order to improve the gas dispersion inside the polymer, a high pressure melt pump and a static mixer are fixed at the end of the extruder barrel to increase the pressure and the residence time of the matter inside the equipment respectively. The filamentary die is cylindrical and its length can be adjusted with a screw to control the pressure drop rate<sup>7</sup>.

### Experimental procedure

Polymer pellets are melted at 190 °C in the feed and the first compression sections of the screw. Carbon dioxide is injected at 150 bar at a constant volumetric flow rate of 0.5 ml/min. After a short period of time, the operating temperature of all the heating jackets placed after the gas injection is gradually decreased down to 143°C, thanks to the viscosity reduction of the polymer/gas solution. The pressure at the die is always adjusted to 300 bar. The foam produced is cooled under ambient conditions or actively cooled by air flushing at the die exit to freeze the foam earlier during its expansion.

## Characterization of foams

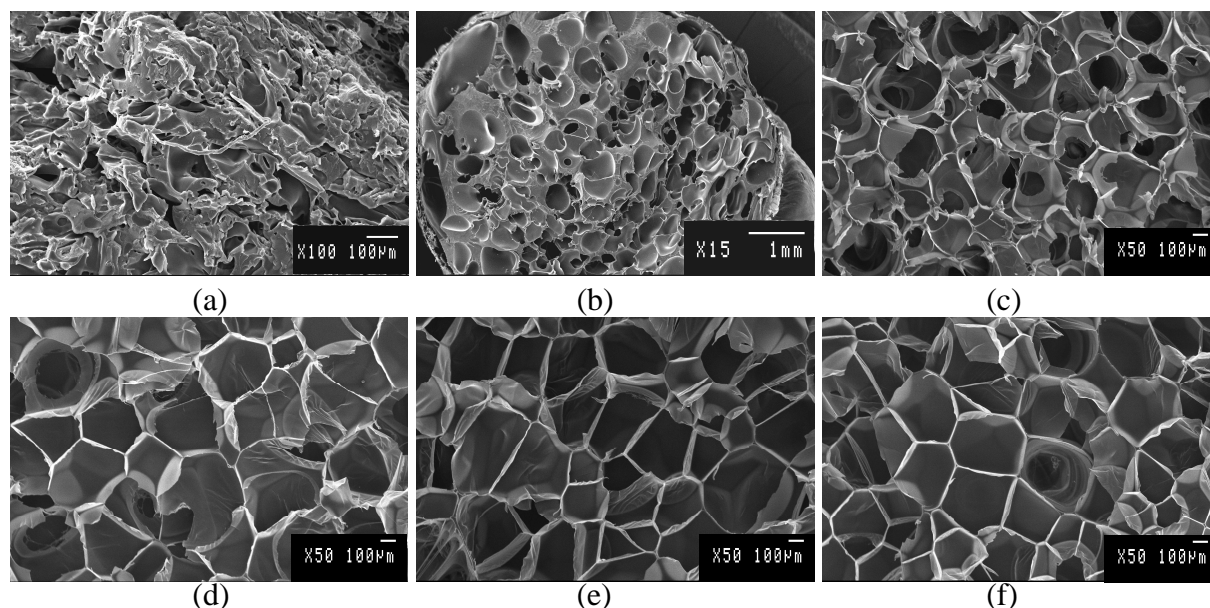
Foams densities were calculated by measuring the weight and volume of the samples. The cell structure was examined by Scanning Electron Microscopy (SEM) with a JEOL JSM 840-A apparatus. The fractured surface was metallized with Pt (30 nm) before observation.

## **II – RESULTS AND DISCUSSION**

We investigated the influence of two experimental parameters on the SAN foam morphology. First, the temperature of the polymer/gas solution has been gradually decreased down to a minimum value of 143 °C in the die, the high pressure melt pump and the static mixer. Below this temperature, the viscosity of the melt becomes too high and the torque of the pump exceeds its maximum value. Under our experimental conditions, about 5 wt % of CO<sub>2</sub> is dissolved into SAN. The foams morphologies analysed by scanning electron microscopy as a function of temperature are presented on figure 2, whereas figure 3 shows the samples produced in the same conditions but directly cooled by air flushing at the exit of the die.

### Effect of die temperature

SAN foams produced at high temperature (180 °C) were very irregular with undefined cell morphologies (figure 2a). Pores seem to have collapsed during foaming. This phenomenon was well described by Park and co-workers<sup>4,8</sup>. At such a high temperature, cells have more time to grow, leading to thinner walls. This favors the diffusion of the gas out of the cells through the very thin walls. As a result, the pressure inside the cells is reduced, and this leads to cell collapse due to the too low melt strength which cannot withstand such porous structure. The foam contraction is visually observable by looking at the extruded foam diameter during the continuous extrusion: the foam first expands and then shrinks rapidly, leading to a poorly foamed sample with a rough skin, which is consistent with the gas escape explanation. The density of this foam is very high (0.8 g/cm<sup>3</sup>) (see figure 4), since the majority of the cells have collapsed.

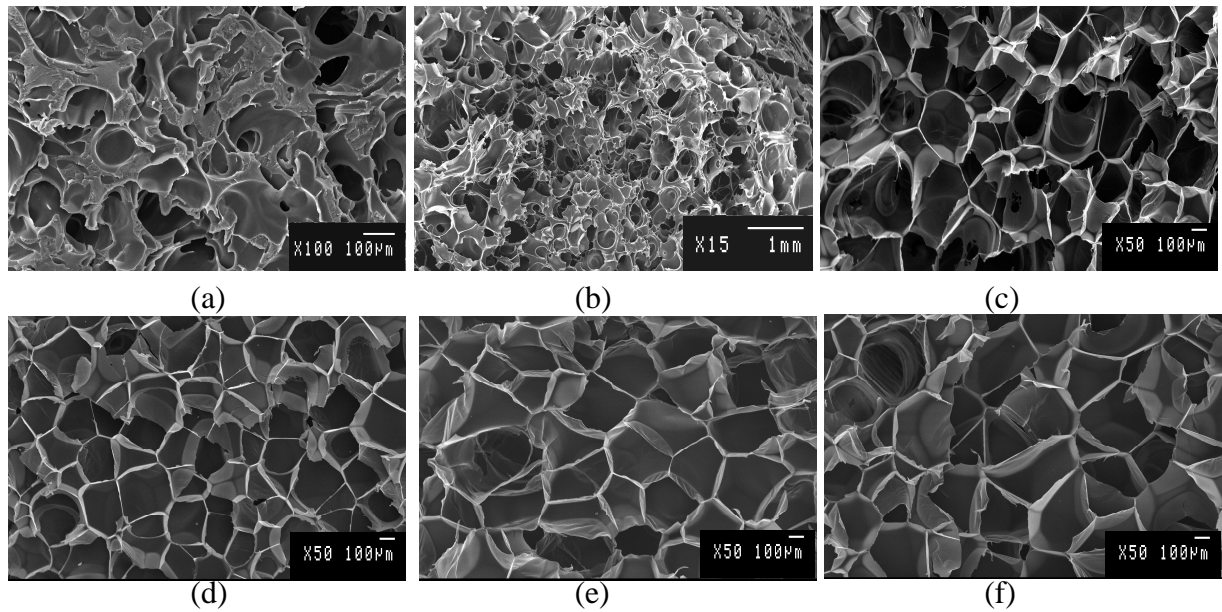


**Figure 2 : Microstructures of SAN foams produced at various extrusion temperatures, without cooling at the end of the extrusion line : (a) 180 °C, (b) 170 °C, (c) 160 °C, (d) 150 °C, (e) 145 °C, (f) 143 °C.**

When the temperature is decreased to 170 °C, pores become more regular as a result of an increase of the melt strength. The cell collapse is thus limited. However, part of the gas still diffuses out of the porous structures as indicated by the rough aspect of the skin foam. This explains the quite high density – 0.5 g/cm<sup>3</sup> – of these foams. Some cells are very big (up to 0.8 mm in diameter), as a result of cell coalescence occurring after a too long cell growth time. The foam produced at 160 °C is characterized by regular pores that are mostly connected to each other, giving rise to an essentially open porosity. This means that the viscosity of the melt solution is not high enough to prevent cell coalescence. The average cell diameter lies around a few hundreds of micrometers. The large decrease of the foam density down to 0.06 g/cm<sup>3</sup> proves that the majority of the injected CO<sub>2</sub> is used for foam expansion and that gas loss through the foam skin is prevented under these conditions (smooth skin). When decreasing the temperature to 150 °C, a well defined porous structure is obtained and no more cell coalescence is detected on the SEM pictures. The cell size goes from 100 to 300 µm and the foam density falls to 0.05 g/cm<sup>3</sup> – the lowest value we reached for SAN. Indeed, a further decrease of temperature to 145 or 143 °C leads to slightly higher foam densities of 0.07 g/cm<sup>3</sup>, with similar foam morphology. This can be explained by a quick freeze of the foam which stops earlier the cell growth. We can estimate the critical volume expansion ratio,  $V_f/V_0$ , for the CO<sub>2</sub>/SAN system, with 5 wt % of gas, considering that 100 % of the gas is used for the foam expansion<sup>8</sup> :

$$\begin{aligned} V_f/V_0 &= (\text{polymer volume} + \text{gas volume})/\text{polymer volume} \\ &= 1 + m_{\text{CO}_2}/m_{\text{SAN}} \times d_{\text{SAN}}/d_{\text{CO}_2} \\ &= 1 + 0.05 \times 1.08/0.0018 \approx 31 \end{aligned}$$

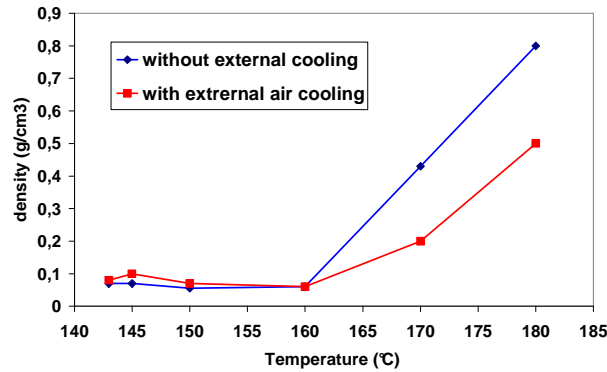
where  $d_{\text{SAN}}$  and  $d_{\text{CO}_2}$ , being the densities of SAN and CO<sub>2</sub> at room temperature, are 1.08<sup>9</sup> and 0.0018<sup>8</sup> respectively. The theoretical maximum expansion ratio calculated is about 31, but in these experiments, we only achieve a maximum of 20-fold increase in SAN volume; this means that not the entirety of CO<sub>2</sub> is used for expanding the foam.



**Figure 3: Microstructures of SAN foams produced at various extrusion temperatures, with air cooling at the end of the extrusion line : (a) 180 °C, (b) 170 °C, (c) 160 °C, (d) 150 °C, (e) 145 °C, (f) 143 °C.**



We can conclude that SAN foams with a regular morphology are obtained when the temperature of the polymer/gas solution is chosen between 150 and 143 °C before foaming. This is due to a higher melt strength that prevents the gas loss and the cell coalescence during foam expansion.



**Figure 4: Density of SAN foams versus die temperature, without and with external cooling.**

### Effect of air cooling

The same experiments were performed with applying an air flush on the extruded foams at the exit of the nozzle in order to limit the gas escape from the foam skin and get rid of foam shrinking after its expansion. An improvement was thus expected at higher melt temperature, when gas loss is obvious. In this context, the effect of air cooling on foam density and cell morphology was studied in the whole temperature range investigated. A striking influence is observed at 180 and 170 °C, as the foam expansion ratio is approximately doubled (figure 4). The freezing of the foam skin has thus allowed to maintain the gas inside the foam thus participating to the cell growth. However, only the external part of the foam was cooled down and no beneficial effect was observed on cell coalescence (figure 9a). Down 170°C, the influence of air cooling on cell morphology is less obvious as a similar density is observed with or without air flush for a same temperature. As seen on figure 4, in the range of 143-150 °C, foam densities were slightly higher under external cooling. This may be explained by a restricted cell growth due to a faster freezing of the foam. This set of experiments shows the huge importance to homogenize the temperature profile in the extrudate.

## **CONCLUSION**

Low-density microcellular SAN foams have been successfully produced in a continuous process using CO<sub>2</sub> as a foaming agent. We studied the effect of a progressive temperature decrease of the polymer/gas solution on the foam morphology, from 180 °C to 143 °C. At high temperature, the produced foams were characterized by a high density as most of the cells collapsed due to the gas escape through the foam skin during expansion. The decrease of the processing temperature progressively suppressed the gas diffusion out of the foam as well as cell coalescence thanks to a higher melt viscosity and foams with regular porosity were obtained in the temperature range of 150-143 °C. We also demonstrated that cooling the extruded foam at the exit of the nozzle with an air flush only reduces gas loss through the foam skin at high temperatures, and allows to prepare foams with low densities.

Nevertheless, this superficial and external cooling was insufficient to prevent cell coalescence during the foam expansion.

Further work will be undergone to investigate the effect of a nanoclay addition on SAN foam morphology.

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### **REFERENCES :**

- [1] LEE, J. W. S.; PARK, C. B.; KIM, S. G., J. Cell. Plastics, Vol. 43, **2007**, p.297
- [2] SUN, H.; SUR, G. S.; MARK, J. E., European Polymer Journal, Vol. 38, **2002**, p. 2373
- [3] DI MAIO, E.; MENSITIERI, G.; IANNACE, S.; NICOLAIS, L.; LI, W.; FLUMERFELT, R. W., Pol. Eng. Sci., Vol. 45, **2005**, p. 432
- [4] NAGUIB, H. E.; PARK, C. B.; REICHELT, N., J. Appl. Pol. Sci., Vol. 91, **2004**, p. 2661
- [5] PARK, C. B.; BALDWIN, D. F.; SUH, N. P., Pol. Eng. Sci., Vol. 35, **1995**, p. 432
- [6] SAUCEAU, M.; NIKITINE, C.; RODIER, E.; FAGES, J., J. Supercrit. Fluids, Vol. 43, **2007**, p. 367
- [7] LEE, J. W. S.; WANG, K.; PARK, C. B., Ind. Eng. Chem. Res., Vol. 44, **2005**, p. 92
- [8] PARK, C. B.; BEHRAVESH, A. H.; VENTER, R. D., Pol. Eng. Sci., Vol. 38, **1998**, p. 1812
- [9] BASF Luran358N Product Data Sheet